

## High Energy Density Cathodes for Next Generation Lithium Ion Batteries

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Lithium ion batteries have revolutionized the portable electronics market, but only 50 % of the theoretical capacity of the currently used layered  $\text{LiCoO}_2$  cathode can be utilized in practical cells due to the chemical and structural instabilities at deep charge and the consequent safety concerns. Also, Co is expensive. In this regard, solid solutions between layered  $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  and  $\text{Li}[\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z]\text{O}_2$  have become appealing recently as they exhibit two times higher capacities than layered  $\text{LiCoO}_2$ . However, these layered oxide solid solutions exhibit an irreversible loss of oxygen from the lattice, huge irreversible capacity loss in the first cycle, and low rate capability. This presentation will focus on a systematic investigation of a number of such high energy density layered oxide solid solutions and viable approaches to reduce the irreversible capacity loss and improve the rate capability. A careful analysis of the first charge and discharge capacity values of a number cathode compositions suggests that part of the oxide ion vacancies formed during the first charge are maintained in the layered lattice during the subsequent discharge-charge cycling in contrast to the idealized literature models involving the elimination of all the oxide ion vacancies from the layered lattice. Surface modification of these layered oxide solid solutions with other materials like alumina and aluminum phosphate is found to be an effective way to reduce the irreversible capacity loss, increase the discharge capacity, and enhance the rate capability. The reduction in irreversible capacity loss and the increase in discharge capacity on surface modification are explained to be due to the retention of more number of oxide ion vacancies in the layered lattice after the first charge compared to that in the unmodified pristine sample. Some of the surface modified cathode compositions offer high capacities of  $\sim 300$  mAh/g compared to the 140 mAh/g realized with  $\text{LiCoO}_2$ , making them appealing for next generation lithium ion batteries. The improved rate capability of the surface modified samples compared to the unmodified samples is attributed to a suppression of the growth of solid-electrolyte interfacial (SEI) layer at the higher operating voltages of up to 4.8 V.

Another approach to increase the energy density is to increase the operating voltage beyond the current cutoff voltage of around 4.3 V, although such strategies will need the development of more robust electrolytes in parallel. In this regard, novel synthesis and characterization of 5 V spinel cathodes and high voltage nano-olivine cathodes will be presented briefly.